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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for Preparing a Polypropylene Wax

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Abstract of the disclosure

Process for preparing a polypropylene wax

Polypropylene waxes of high crystallinity and good processibility can be obtained by solution polymerization at a temperature above 110°C, if a catalyst system, which has been formed from a magnesium-alkoxy compound, a tetravalent titanium compound, a silicon compound and an aluminumorganic compound, is used in the polymerization. The polypropylene waxes prepared by the process are viscous-hard, colorless, non-tacky, heat-stable, readily grindable products having an isotacticity, determined by IR-spectroscopy, of more than 70 % and a melt viscosity of 50 to 4000 mPa.s, measured at 170°C. The waxes are suitable, for example, as base masses for pigment preparation, for an abrasion-resistant finish of printing inks, for dulling paints, as an aid in the processing of plastics, for example as lubricants and release agents, as a formulation component in photographic toners and as agents for increasing the melting point.

HOECHST AKTIENGESELLSCHAFT HOE 92/F 241 Dr.DA/-

Description

Process for preparing a polypropylene wax

The invention relates to a process for preparing polypropylene waxes of high crystallinity by homopolymerization of propylene or copolymerization of propylene with a small fraction of other olefins, to the catalyst used for this purpose and to the waxes prepared by this process.

It is known that the polymerization of propylene in the presence of a catalyst, obtained by reacting a titanium compound with a magnesium compound, at a relatively high temperature leads to waxy polymers having a comparatively high melt viscosity (cf. DE 2,329,641). The crystallinity of these waxes is in the lower to medium range and can be influenced within certain limits by the nature of the aluminum-organic compound used for activation, but at most only moderate degrees of crystallinity are obtained.

Moreover, highly crystalline poly-1-alkene waxes, in particular polypropylene waxes, are accessible by using a specific catalyst system composed of the reaction product of titanium tetrahalide, magnesium alcoholate and an ether, alcohol, amine or a carboxylic acid or a carboxylic acid derivative (cf. DE 3,148,229). Additionally, a further, stereoregulating component selected from the group comprising carboxylic acid esters, phosphoric acid amides, ethers or thioethers is added during the polymerization. The polymerization is carried out in solution in a temperature range from 100 to 110°C. At a higher polymerization temperature, the crystallinity of the products decreases. A disadvantage of this process is that the required low polymerization temperatures are as a rule below the cloud point of the waxes formed, so that the latter precipitate and hence cause the formation of undesired deposits in the reactor.

Finally, a process for the preparation of "exclusively isotactic" polypropylene waxes by bulk polymerization with the aid of a titanium halide and an aluminum-organic compound at a temperature in the range from 180 to 350°C and a pressure from 500 to 3000 bar is known (cf. DE 3,431,842). The process involves a high energy consumption and requires expensive pressure- and temperature-resistant equipment.

In addition, the preparation of highly isotactic homopolymeric and copolymeric polypropylene waxes by a gas phase process is known, in which supported catalysts containing titanium and magnesium are used in combination with aluminum-organic activators and electron donors such as, for example, alkoxysilane compounds (cf. DE 4,030,379). The products accessible by this process are, however, comparatively high-molecular. Their further processing by the melt technology, which is usual for waxes and presupposes low viscosities, is not possible with these, or at least difficult.

It is also known that polypropylene waxes can be prepared with the aid of soluble catalyst systems containing metallocene compounds (cf. DE 3,743,321, DE 3,904,468 and DE 3,743,320). The synthesis and handling of the metallocene components and especially of the aluminoxane components used as co-catalysts in a large excess is expensive.

It has now been found that polypropylene waxes of high crystallinity and good processibility can be obtained by solution polymerization at a temperature above 110°C, if a specific catalyst system in combination with a silicon compound is used in the polymerization.

The invention therefore relates to a process for preparing a polyolefin wax having an IR isotacticity of > 70 % and a melt viscosity of 50 to 4000 mPa.s, measured at 170°C, by homopolymerization of propylene or copolymerization of propylene with 0.1 to 5 % by weight of ethylene

or of an olefin of the formula $R-CH=CH_2$, in which R is an alkyl radical having 2 to 38 carbon atoms, in solution at a temperature of $\geq 110°C$ at a pressure of 2 to 100 bar in the presence of a catalyst system composed of a titanium-containing component A, a silicon-containing component B and an aluminum-organic component C, wherein component A has been prepared by reacting a magnesium compound of the formula I

$$Mg(OR^1)_nX_{2-n} \quad (I),$$

in which R^1 is identical or different C_1-C_{10}-alkyl radicals, X is a halogen atom and n is 1 or 2, with a tetravalent titanium compound of the formula II

$$Ti(OR^2)_mX_{4-m} \quad (II),$$

in which R^2 is identical or different C_1-C_6-alkyl radicals, X is a halogen atom and m is a number from 0 to 4,
a silicon compound of the formula III

$$R^3_pSi(OR^4)_{4-p} \quad (III)$$

in which p is 1, 2 or 3, R^3 is identical or different C_1-C_{16}-alkyl radicals and R^4 is identical or different C_1-C_{16}-alkyl radicals or unsubstituted or alkyl-substituted C_5-C_8-cycloalkyl radicals, C_6-C_{18}-aryl radicals or C_7-C_{18}-aralkyl radicals, is used as component B and
an aluminum compound of the formula IV

$$R^5_qAlCl_{3-q} \quad (IV)$$

in which q is 1, 2 or 3 and R^5 is identical or different C_1-C_{30}-alkyl radicals, is used as component C.

The preparation of the catalyst is carried out in such a way that initially the catalyst component A is prepared by reacting a magnesium compound, preferably a magnesium alcoholate, with a tetravalent titanium compound, preferably a titanium tetrahalide, in an inert solvent. The magnesium alcoholate used is a compound of the formula I

$$Mg(OR^1)_nX_{2-n}$$

(I),

in which R^1 is identical or different, preferably straight-chain C_1-C_{10}-alkyl radicals, preferably C_1-C_6-alkyl radicals, X is a halogen atom and n is 1 or 2. $Mg(OCH_3)_2$, $Mg(OC_2H_5)_2$, $Mg(OC_3H_7)_2$ and $Mg(OC_4H_9)_2$ may be mentioned as examples. However, magnesium alcoholates of the formula $MgX(OR^1)$, in which X is halogen and R^1 is as defined above, can also be used.

The magnesium compound is reacted with a tetravalent titanium compound of the formula II

$$Ti(OR^2)_mX_{4-m}$$

(II),

in which R^2 is identical or different C_1-C_6-alkyl radicals, X is a halogen atom and m is a number from 0 to 4, at a temperature from 0 to 200, preferably 20 to 120°C. The reaction medium used is an inert diluent and suspending agent, for example a hydrocarbon. Aliphatic and cycloaliphatic hydrocarbons such as, for example, hexane, heptane or cyclohexane and also aromatic hydrocarbons such as benzene, toluene etc. are suitable. Advantageously, the magnesium component is introduced as a suspension, and the titanium compound is added with stirring. The magnesium compound and titanium compound are expediently and preferably used in a molar ratio of 1 : 0.2 to 1 : 5, but molar ratios outside this range are also possible. The reaction times are in general between 1 and 10 hours.

The catalyst component A thus obtained arises as a solid. It is freed of soluble fractions by repeated washing with an inert hydrocarbon, preferably with the medium used in its preparation. The washed catalyst can, if desired, be reacted with an electron donor. Suitable electron donors are alcohols such as methanol, ethanol and propanol, ethers such as diethyl ether, di-n-butyl ether or di-i-amyl ether, amines such as triethylamine, aliphatic or aromatic carboxylic acids and derivatives thereof, for example esters, anhydrides, halides or amides such as, for example, ethyl acetate, ethyl benzoate, benzoic anhydride and benzamide.

The component B used is a silicon compound of the formula III

$$R^3_pSi(OR^4)_{4-p} \qquad (III),$$

in which p is 1, 2 or 3, R^3 is identical or different C_1-C_{16}-alkyl radicals, for example methyl, ethyl or n- or i-propyl, and R^4 is identical or different C_1-C_{16}-alkyl radicals or unsubstituted or alkylsubstituted C_5-C_8-cycloalkyl radicals, C_6-C_{18}-aryl radicals, for example phenyl radicals, or C_7-C_{18}-aralkyl radicals, for example 4-methylphenyl radicals. Methyltrimethoxysilane, ethyltrimethoxysilane, propyltrimethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, isobutylmethyldimethoxysilane, trimethylmethoxysilane, cyclopentylmethyldimethoxysilane, cyclohexylmethyldimethoxysilane, phenyltrimethoxysilane and diphenyldimethoxysilane may be mentioned as examples of component B.

As the aluminum-organic component C, compounds of the formula IV

$$R^5_qAlCl_{3-q} \qquad (IV)$$

are used, in which q is 1, 2 or 3 and R^5 is identical or different C_1-C_{30}-alkyl radicals, preferably C_2-C_{12}-alkyl

radicals. The Cl/Al atomic ratio is accordingly between 2 : 1 and 0 : 1. Preferably, a ratio between 1 : 1 and 0.25 : 1 is set, which can be effected by mixing aluminum-organic compounds of different chlorine content, for example triethylaluminum and diethylaluminum chloride.

Using the catalyst system according to the invention, propylene or propylene with 0.1 to 5 % by weight of ethylene or an olefin of the formula $R-CH=CH_2$, in which R is an alkyl radical having 2 to 38 carbon atoms, for example 1-butene or 1-hexene, are polymerized.

The procedure for carrying out the polymerization is advantageously such that the catalyst system is first prepared by reacting component C with component B by mixing in the presence of an inert hydrocarbon and then adding component A to this mixture. The quantities are to be selected here in such a way that the component C (relative to aluminum)/component B molar ratio is 200 : 1 to 1 : 1, preferably 50 : 1 to 10 : 1, and the component C (relative to aluminum)/component A (relative to titanium) molar ratio is 1 : 1 to 30 : 1, preferably 2 : 1 to 20 : 1.

The polymerization is carried out continuously or discontinuously in solution at a temperature above 110°C, preferably between 115 and 150°C, particularly preferably between 120 and 140°C, at a pressure of 2 to 100 bar, preferably 5 to 20 bar. It is also possible to polymerize in inert hydrocarbons which are liquid at the polymerization temperature but solid at room temperature.

The molecular mass is regulated in the known manner by addition of hydrogen. After completion of the polymerization, the solvent is separated off, preferably by distillation, if necessary after prior decomposition of the catalyst with suitable decomposing agents, for example water, and subsequent filtration.

The polyolefin waxes prepared by the process according to the invention are viscous-hard, colorless, non-tacky, heat-stable, readily grindable products having a degree of isotacticity, determined by IR spectroscopy, of more than 70 % and a melt viscosity of 50 to 4000 mPa.s, measured at 170°C. The waxes are suitable, for example, as base masses for pigment preparation, for an abrasion-resistant finish of printing inks, for dulling paints, as an aid in the processing of plastics, for example as lubricants and release agents, as a formulation component in photographic toners and as agents for increasing the melting point.

The examples which follow serve to explain the invention in more detail.

The melt viscosities were measured in a rotary viscometer. The determination of isotacticity was carried out by IR spectroscopy according to J.P. Luongo, J. Appl. Pol. Chem. 3 (9), 302 (1960), and the heat of fusion was determined by DSC spectroscopy.

Example 1

114.4 g (1.0 mol) of magnesium ethylate were suspended in 1000 cm^3 of a diesel oil fraction (boiling range 140 to 160°C). 284.8 g (1.5 mol) of titanium tetrachloride were added dropwise to the batch with stirring at 85°C in the course of 4 hours. The suspension was then stirred for a further 30 minutes at 85°C. The precipitate was washed by repeated stirring with diesel oil, until the supernatant diesel oil above the solid was free of titanium.

The catalyst system used for the polymerization was prepared by mixing 150 mmol of triethylaluminum, 75 mmol of diethylaluminum chloride (catalyst component C) and 7.5 mmol of cyclohexylmethyldimethoxysilane (component B) in 1.5 dm^3 of diesel oil fraction and subsequently stirring 30 mmol (relative to Ti) of the above catalyst

component A into this mixture. The molar ratio of the said components was 5 : 2.5 : 0.25 : 1.

15 dm^3 of a diesel oil fraction (boiling range 140 to 160°C) were introduced into a 40 dm^3 vessel with impeller stirrer. After heating of the vessel contents to 130°C, hydrogen gas was first added up to an internal pressure of 0.1 bar, and then propylene up to an internal pressure of 5 bar. 0.5 dm^3 of the catalyst described above was pumped in at 130°C. By continuous further addition of 3.2 kg of propylene and 0.5 dm^3 of hydrogen per hour and intermittent addition of catalyst, the pressure was maintained at 5 bar. The polymerization temperature was 130°C.

After 75 minutes, a total of 1050 cm^3 of the catalyst suspension, corresponding to about 21 mg atom of Ti, had been consumed. The reaction was stopped by addition of 15 cm^3 of water, the polymer solution was filtered and the solvent was distilled off in vacuo. This gave 3.55 kg of polypropylene wax.

Melt viscosity at 170°C 1330 mPa.s; heat of fusion 83 J/g; IR isotacticity 72 %.

Comparison Example 1

The catalyst component A was prepared according to Example 1. The catalyst system used for polymerization was composed of 90 mmol of triethylaluminum, 60 mmol of diethylaluminum chloride and 30 mg atom of component A. A silicon compound was not used.

The polymerization of propylene under the conditions described in Example 1 led to a wax product which had a lower crystallinity than that obtained according to Example 1.

Melt viscosity at 170°C: 1320 mPa.s; heat of fusion

63 J/g; IR isotacticity 63 %.

Comparison Example B

A polymerization catalyst was prepared according to DE-A 3,148,229, Example 1. For this purpose, 114.4 g (1.0 mol) of magnesium ethylate were suspended in 1000 cm^3 of a diesel oil fraction (boiling range 140 - 160°C). 380 g (2.0 mol) of titanium tetrachloride were added dropwise with stirring at 85°C in the course of 4 hours. The batch was then stirred for a further 30 minutes at 85°C. The precipitate was washed by decanting and repeated stirring with diesel oil, until the diesel oil supernatant above the solid was free of titanium.

31.7 g (0.20 mol) of di-isoamyl ether as an electron donor were then added to the suspension, and the mixture was stirred for 1 hour at 100°C. The solid was freed of soluble titanium compounds by washing with diesel oil.

Using this catalyst, propylene was polymerized according to Example 1 of DE-A 3,148,229, but a polymerization temperature of 130°C was chosen in place of the indicated 100°C. The resulting polypropylene wax showed the following characteristic data:
Melt viscosity at 170°C 810 mPa.s; heat of fusion 79 J/g; IR-isotacticity 71 %.
As can be seen, the isotacticity value of the wax is markedly lower than that of a product prepared in the same manner but at 100°C (85 %). If the polymerization is carried out at 100°C according to DE 3,148,229, the isotacticity value is admittedly higher, but the inner wall of the polymerization vessel shows deposits of precipitated product, which impede the removal of the heat of reaction.

Example 2

The polymerization was carried out according to Example 1. The catalyst was prepared by mixing 210 mmol of triethylaluminum, 105 mmol of diethylaluminum chloride, 22.5 mmol of cyclohexylmethyldimethoxysilane and 30 mg atom of the catalyst component A from Example 1, corresponding to a molar ratio of 7 : 3.5 : 0.75 : 1. This gave a polypropylene wax having the following characteristic data:
Melt viscosity at 170°C 1990 mPa.s; heat of fusion 106 J/g; IR isotacticity 80 %.

Example 3

114.4 g of magnesium ethylate were suspended in 1000 cm^3 of a diesel oil fraction (boiling range 140 to 160°C). 380 g (2.0 mol) of titanium tetrachloride were added dropwise to the batch with stirring at 85°C in the course of 4 hours. The suspension was then stirred for a further 30 minutes at 85°C. The precipitate was washed by repeated stirring with diesel oil, until the diesel oil supernatant above the solid was free of titanium.

31.7 g of diisoamyl ether (200 mmol) were then added to the suspension, and the mixture was stirred for 1 hour at 100°C. The solid was again freed of soluble titanium compounds by washing with diesel oil. It still contained 3.5 % of the titanium originally introduced as titanium tetrachloride.

The polymerization was carried out according to Example 1. The catalyst system was prepared by mixing 210 mmol of triethylaluminum, 105 mmol of diethylaluminum chloride, 22.5 mmol of cyclohexylmethyldimethoxysilane and 30 mg atom of catalyst component A, corresponding to a molar ratio of 7 : 3.5 : 0.75 : 1. This gave a polypropylene wax having the following characteristic data:
Melt viscosity at 170°C 1200 mPa.s; heat of fusion

110 J/g; IR isotacticity 84 %.

Example 4

The catalyst system used for the polymerization was prepared analogously to Example 1, diphenyldimethoxysilane being used in place of cyclohexylmethyldimethoxysilane. The polymerization of propylene, carried out as described in Example 1, gave a wax having the following characteristic data:
Melt viscosity at 170°C 1600 mPa.s; heat of fusion 82 J/g; IR isotacticity 73 %.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for preparing a polypropylene wax having an IR isotacticity of > 70 % and a melt viscosity of 50 to 4000 mPa.s, by homopolymerization of propylene or copolymerization of propylene with 0.1 to 5 % by weight of ethylene or of an olefin of the formula $R-CH=CH_2$, in which R is an alkyl radical having 2 to 38 carbon atoms, in solution at a temperature of ≥ 110°C at a pressure of 2 to 100 bar in the presence of a catalyst system composed of a titanium-containing component A, a silicon-containing component B and an aluminum-organic component C, wherein component A has been prepared by reacting a magnesium compound of the formula I

$$Mg(OR^1)_nX_{2-n}$$

(I),

in which R^1 is identical or different C_1-C_{10}-alkyl radicals, X is a halogen atom and n is 1 or 2, with a tetravalent titanium compound of the formula II

$$Ti(OR^2)_mX_{4-m}$$

(II),

in which R^2 is identical or different C_1-C_6-alkyl radicals, X is a halogen atom and m is a number from 0 to 4,
a silicon compound of the formula III

$$R^3_pSi(OR^4)_{4-p} \qquad \text{(III)}$$

in which p is 1, 2 or 3, R^3 is identical or different C_1-C_{16}-alkyl radicals and R^4 is identical or different C_1-C_{16}-alkyl radicals or unsubstituted or alkyl-substituted C_3-C_8-cycloalkyl radicals, C_6-C_{18}-aryl radicals or C_7-C_{18}-aralkyl radicals, is

used as component B and
an aluminum compound of the formula IV

$$R^5_qAlCl_{3-q} \qquad (IV)$$

in which q is 1, 2 or 3 and R^5 is identical or different C_1-C_{30}-alkyl radicals, is used as component C.

2. The process as claimed in claim 1, wherein the reaction of the magnesium compound of the formula I with the titanium compound of the formula II has been carried out in the presence of an electron donor from the group comprising ethers, alcohols and carboxylic acids and derivatives thereof.

3. A catalyst system for preparing a polyolefin wax having an IR isotacticity of > 70 % and a melt viscosity of 50 to 4000 mPa.s, measured at 170°C, composed of a titanium-containing component A, a silicon-containing component B and an aluminum-organic component C, wherein component A has been prepared by reacting a magnesium compound of the formula I

$$Mg(OR^1)_nX_{2-n}$$

(I),

in which R^1 is identical or different C_1-C_{10}-alkyl radicals, X is a halogen atom and n is 1 or 2, with a tetravalent titanium compound of the formula II

$$Ti(OR^2)_mX_{4-m}$$

(II),

in which R^2 is identical or different C_1-C_6-alkyl radicals, X is a halogen atom and m is a number from 1 to 4,
component B is a silicon compound of the formula III

$$R^3_pSi(OR^4)_{4-p} \qquad (III)$$

in which p is 1, 2 or 3, R^3 is identical or different C_1-C_{16}-alkyl radicals and R^4 is identical or different C_1-C_{16}-alkyl radicals or unsubstituted or alkyl-substituted C_5-C_8-cycloalkyl radicals, C_6-C_{18}-aryl radicals or C_7-C_{18}-aralkyl radicals, and component C is an aluminum compound of the formula IV

$$R^5_qAlCl_{3-q} \qquad (IV)$$

in which q is 1, 2 or 3 and R^5 is identical or different C_1-C_{30}-alkyl radicals.

4. The catalyst system as claimed in claim 3, wherein component A has been prepared from titanium tetrachloride, a magnesium alcoholate of the formula $Mg(OR^1)_2$, in which R^1 is a C_1-C_6-alkyl group, and a silicon compound of the formula IV is used.

5. A polyolefin wax having an IR isotacticity of > 70 % and a melt viscosity of 50 to 4000 mPa.s, measured at 170°C, obtained as claimed in claim 1.